

A preliminary ^{29}Si MAS NMR study of Mg_2SiO_4 ringwoodite and wadsleyite

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Mg_2SiO_4 -rich ringwoodite and wadsleyite are considered to be the dominant minerals in the mantle transition zone. An important factor that may significantly influence their phase boundaries is Mg-Si order/disorder. This has been examined in several single-crystal X-ray diffraction studies, although this technique is intrinsically insensitive to small amounts of Mg-Si disorder. We have applied ^{29}Si NMR to shed further light on this issue. ^{29}Si NMR is known to yield distinct peaks in the range of -60 to -120 ppm for tetrahedral Si (Si[4]), and -160 to -220 ppm for octahedral Si (Si[6]) in silicate minerals, and is thus ideal for revealing and quantifying small amounts of Mg-Si disorder in these minerals.

High-pressure samples were synthesized using a Kawai-type multi-anvil apparatus at 900 to 1600 C and high pressures near the ringwoodite-wadsleyite boundary. The starting material was Mg_2SiO_4 forsterite synthesized by the sol-gel method. ^{29}Si MAS NMR spectra were obtained using a Varian 400 Unity-Inova spectrometer at a resonance frequency of 79.5 MHz for ^{29}Si , and a Doty 4 mm CP-MAS probe. The ^{29}Si chemical shift is referenced to an external standard of tetramethyl silane (TMS). The ^{29}Si spin-lattice relaxation time (T1) was measured using the saturation-recovery method.

The ^{29}Si MAS NMR spectrum of the starting material contains a single peak at -61.7 ppm with a FWHM of 16 Hz (0.2 ppm) attributable to forsterite, and no other peaks that may indicate impurity phases. The ^{29}Si T1 of forsterite was about 500 s.

Two samples of ringwoodite were used for NMR measurement: One was actually three samples combined that were synthesized at 900 to 1000 C (total 60 mg); the other was synthesized at 1600 C (4.6 mg). The ^{29}Si NMR spectra for both are similar: There is a major peak at -81.3 ppm with a FWHM of 15 Hz, and a broader peak near -61.7 ppm with a FWHM of 42 Hz. The former can be attributed to ringwoodite and the latter to untransformed forsterite due to temperature gradient. The T1 for ringwoodite was about 20 s, much shorter than forsterite. The peak for the untransformed forsterite is broader than the starting material, possibly due to extensive defects developed during low-temperature compression. In addition, there are two small partially resolved peaks of nearly equal intensities to the less negative chemical shift side of the strong -81.3 ppm peak, at -80.3 and -80.0 ppm with a FWHM of 19 and 41 Hz, respectively. These peaks cannot be ascribed to any known magnesium silicates, and may be due to structural defects in ringwoodite. They are unlikely, though, to be associated with Si-Mg disorder, because replacement of a Mg by Si[6] is expected to result in a more negative chemical shift for the neighboring Si[4] due to increased shielding. There is also a small sharp peak near -78.7 ppm for the 900 to 1000 C sample, attributable to a small amount of wadsleyite. We observed no peaks in the -160 to -220 ppm region expected for Si[6] for either sample. The abundance of Si[6] in ringwoodite is estimated to be below 0.5% for the larger 900 to 1000 C sample, and below 2% for the 1600 C sample.

The ^{29}Si MAS NMR spectrum for a wadsleyite sample synthesized at 1600 C contains a symmetric peak at -78.7 ppm with a FWHM of 27 Hz attributable to wadsleyite, and a broader peak at -60.9 ppm attributable to untransformed forsterite. There is also a small peak at -81.3 ppm due to a small amount of ringwoodite. The T1 for wadsleyite was about 55 s. Again no peaks in the -160 to -220 ppm region were observed, suggesting that Si[6] in wadsleyite may be below 2%.

In summary, we have found no evidence for Si-Mg disorder in ringwoodite and wadsleyite. These results are preliminary, and will be further constrained by collecting higher-quality NMR data on ^{29}Si -enriched samples and by reducing the temperature gradient in the high-pressure assembly. The latest results will be presented at the meeting.